

Aqueous emulsion containing fluoros cobalt species in supercritical CO₂ for catalytic air oxidation of toluene

Jie Zhu, Alan Robertson and Shik Chi Tsang*

Surface and Catalysis Research Centre, Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK. E-mail: s.c.e.tsang@reading.ac.uk

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An aqueous emulsion containing ionic Co²⁺ and Br⁻ species stabilised by fluorosurfactant-like species in supercritical CO₂-air mixture acts as a nano-reactor with excellent interfacial contacts of all necessary hydrophilic/hydrophobic species, which renders safe operation of catalytic aerial oxidation of toluene at high yields.

Selective catalytic partial oxidation of alkylaromatics to acids by air or molecular oxygen is of great economic and industrial importance.¹ The key challenges regarding the development of new catalytic processes in this area include the identification of active and particularly selective catalyst species (unselective attacks on C–C or aromatic C–H bonds should be avoided), ease of separation of product and catalyst and safe operation of the highly exothermic oxidation reactions. Many attempts have been made at developing solid catalysts containing transition metal ions. However, poor activity and selectivity and problems with catalyst stability presently excludes them from existing applications. Currently, the principal industrial methods employ simple cobalt salts as homogeneous catalysts in an air pressurised aqueous–acetic acid mixture in the presence of ionic promoter(s) (Mn ions and/or bromide).² The acetic acid–water mixture is apparently crucial in providing the solvent medium for the free and effective interactions between ionic catalyst and promoter species and the organic substrates. However, problems with decarboxylation of the solvent and products due to the unselective oxidation, use of extremely corrosive and toxic acetic acid, difficulty in solvent and catalyst recovery, and explosion hazards associated with solvent and dioxygen at high concentration (with reported explosions) are obvious.³ With increasingly demanding environmental legislation, public and corporate pressure, a new process is urgently required.⁴ Supercritical carbon dioxide (scCO₂) has recently received considerable attention as a new versatile, environmentally friendly medium for a variety of catalytic reactions; these include free-radical polymerization,⁵ hydroformylation,⁶ hydrogenation,⁷ and partial oxidations.⁸ Its non-toxic, non-combustible and non-flammable nature combined with the ease of solvation of some organic substrates in the inexpensive medium and ease of pressure facilitated separation may offer an exciting possibility of replacing acetic acid for catalytic partial oxidations. Despite these encouraging facts, the major limitation is its inability to dissolve hydrophiles, in particular ionic catalyst/promoter species that are required for the oxidation (Co²⁺/NaBr). Recent work has shown that a number of fluorosurfactants were able to form aqueous microemulsions in scCO₂.⁹ Similarly, other fluorosurfactant related species can also modify the interfacial tension of the scCO₂ forming a metastable aqueous emulsion therein.¹⁰ Thus, fluorosurfactants and related compounds are able to disperse water-soluble metal salts in the nonpolar scCO₂ medium.

Here we report a new approach for oxidation of toluene by dioxygen based on emulsion catalysis in supercritical CO₂ using fluorosurfactant-tagged Co(II)/NaBr in a water–scCO₂ mixture (the fluorosurfactant tag and scCO₂ solvent contain no C–H for possible non-selective attacks). Extremely high conversion (>99%), high selectivity to benzoic acid (>99% with traces of benzaldehyde and benzyl alcohol), and high turnover fre-

quencies (TOF = 6.19 × 10⁻³ s⁻¹) were achieved without the use of acetic acid. The nature of the emulsion droplet (nano-reactor) containing Co²⁺/NaBr (allowing excellent interfacial contacts between non-polar substrate molecules and ionic catalytic species) coupled with the intrinsic advantages of supercritical CO₂ [low viscosity, high diffusivity, rapid product desorption, and complete miscibility of substrates (alkylaromatics and dioxygen in particular)] enables a fast oxidation reaction to be sustained.

Experiments were carried out in a 160 ml stainless steel autoclave (with Teflon cup insert reducing the volume to ca. 111 ml) equipped with an overhead stirrer. 0.25 mmol [CF₃(CF₂)₈COO]₂Co·nH₂O denoted as F-Co,† 0.2 mmol NaBr and a small quantity of H₂O (100 μl unless otherwise specified) were added to the autoclave that hosted a small internal container holding 18.8 mmol toluene liquid (in order to avoid its direct liquid-phase reaction with the catalyst). The autoclave was charged with 10 bar O₂ and topped up to 150 bar by pumping CO₂ into the autoclave at 120 °C. The amount of toluene used was readily soluble under these conditions.¹¹ The autoclave was connected to a GC for on-line monitoring of reaction mixtures intermittently. All products were analyzed quantitatively using GC and HPLC after 12 h.

The non-fluorous cobalt catalyst (Co(II) acetate/NaBr) that is known to be extremely active in the oxygen pressured acetic acid–water system, was found to be inert (conv. 0.1%) due to its insolubility in CO₂–water (monitored through sapphire windows). In contrast, F-Co/NaBr showed excellent activity (conv. 98.2% with selectivity to benzoic acid of 99.1%). It was interesting to find that the F-Co showed a relatively poor activity when either NaBr or water (using dehydrated F-Co) was not included (conv. 6.0 and 14.2%, respectively). These results clearly indicate that F-Co, NaBr and H₂O are all essential components for effective catalysis. Variation of the quantity of water added (100, 200, 300, 500 μl) to the F-Co/NaBr was then investigated (Fig. 1). The activity curves all show a general induction period followed by a rapid increase in activity. It is interesting that the induction period was shortened in accordance with increasing quantity of water added. It is well documented that formation of emulsion assemblies depend on the quantity and ratio of water to surfactant used (*W*) in organic solvent. It is also known that scCO₂ can dissolve water in its phase. Some water is therefore needed to saturate the scCO₂ phase before emulsion droplets can form.^{9a} Thus, our results suggest that emulsions may not form straight away if insufficient amounts of water are present during the induction period (poor solid/CO₂ interface due to lack of water). However, oxidation of toluene will yield additional quantities of

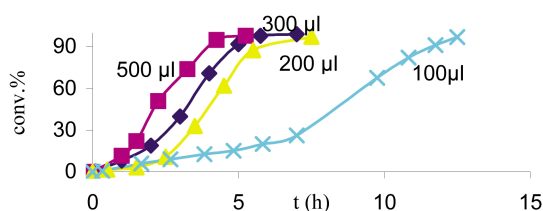


Fig. 1 The effect of water on catalytic activity.

water (by-product) to assist emulsion formation at a later stage. It is not yet known whether a truly stable microemulsion or a coarsely dispersed biphasic system is involved. However, as far as catalysis is concerned, once the emulsion is established, it can account for the abrupt increase in activity after the induction period. Based on the activity curves, we estimate that a minimum of 270–310 μl water (the amount of water added plus the envisaged amount of water produced from reaction at the end of the induction period) is required before the emulsion is formed. Despite the actual water solubility depending on conditions and impurities (substrates and products) in scCO_2 this value is in a good agreement with Wiebe's calculations.¹² The corrected W_o values of water to fluoros Co(II) ratios after deducing the amount water required to saturate the scCO_2 from 0–44. The effects of P_{O_2} , toluene, NaBr, P_{CO_2} (total P), and temperature on activity were briefly studied. From Table 1, a critical quantity of NaBr seems to be required (>0.05 mmol) for high activity. Once above this value the activity remains virtually the same. This is consistent with the literature where; a small quantity of Br^- acts as ionic promoter to facilitate rapid electron transfers of the catalytic Co species (II and III). The activity observed follows a first order rate with respect to toluene added suggesting the C–H activation in the toluene oxidation is likely to be the rate limiting step as is typical in most alkane oxidations.¹ Activity was found to be independent of P_{O_2} (23.1–46.2 mmol, rendering O_2 in excess), which reflects ease of availability of O_2 for the catalytic sites (miscible in scCO_2 with excellent diffusivity) in scCO_2 . It is also interesting that a higher rate was achieved with lower P_{CO_2} (toluene confirmed to be solubilized at all conditions), which may be attributed to higher diffusivity and/or a greater concentration of toluene at lower applied pressures. The excellent TOFs were recorded at 80 °C ($9.15 \times 10^{-4} \text{ s}^{-1}$), 100 °C ($2.86 \times 10^{-3} \text{ s}^{-1}$) and 120 °C ($6.48 \times 10^{-3} \text{ s}^{-1}$) and the apparent activation energy of this catalysed oxidation reaction by this new system was estimated to be 49.82 kJ mol⁻¹. Our un-optimized catalyst, evaluated at 100 °C ($2.86 \times 10^{-3} \text{ s}^{-1}$) gave an activity for toluene oxidation which was more than 10 times higher than the reported rate of $2.4 \times 10^{-4} \text{ s}^{-1}$ (87 °C) in acetic acid–water^{2a} and 100 times higher than the solid Co counterpart in scCO_2 ($1 \times 10^{-5} \text{ s}^{-1}$ at 140–200 °C¹¹). Although the differences of these rates should not be taken too literally, the excellent activity of our emulsion catalyst in water– scCO_2 is apparent. Such high activity can be attributed to the intrinsically faster transfers in water– scCO_2 than in liquid, the dynamic properties of emulsion and the local high concentration of ingredients in the emulsion droplets. Importance of the fluoros anion for aqueous emulsion formation is clearly demonstrated in Fig. 2. The F–Mg (replacing F–Co) blended with Co acetate (0.25 mmol) plot shows similar activity to the F–Co. This result suggests that cationic species are likely to be mobile (within the droplet) despite their difference in binding with the fluoros anion (compare mp values). It is therefore unnecessary to directly fluorinate the Co species as the inexpensive cobalt acetate is equally effective when in combination with fluoros anions. F–K/Co acetate achieved comparable conversions though over a greater period of time (Fig. 2). The precise reason for this is not yet known.

Table 1 Effect of experimental parameters on catalytic activity

Variable ^a	TOF ($\times 10^3 \text{ s}^{-1}$)	Variable ^a	TOF ($\times 10^3 \text{ s}^{-1}$)
P_{O_2} /bar	5	3.94	NaBr/mmol
	7.5	3.94	2
	10	3.96	1.10
Toluene/mmol	0.2	0.50	5
	0.5	1.40	3.40
	0.8	1.98	10
	1.5	3.96	3.97
			20
		Total P /bar	100
			6.30
			150
			3.96
			170
			3.33

^a Normal conditions: 10 bar O_2 , topped up with scCO_2 to 150 bar, NaBr (0.2 mmol), toluene (14.1 mmol), H_2O (400 μl) and F–Co (0.25 mmol) at 120 °C, only one variable specified above was altered.

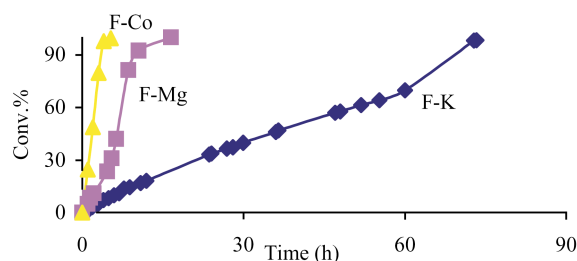


Fig. 2 The effect of cation on catalytic activity.

However, it can be postulated that interactions of the fluoros anions with scCO_2 /water to form emulsions may be kinetically slower in order to override the stronger ionic interactions within this solid (reflected by its higher mp). The extremely small size of the emulsion droplets in scCO_2 are reflected in a detailed postmortem analysis of the catalyst following a rapid depressurisation of the system (F–Co(II)/NaBr/400 μl H_2O) from typical conditions to give a solid foam. TEM micrographs of this foam (not shown) indicate extremely well dispersed NaBr crystallites of 3 ± 1 nm in the non-crystalline fluoros Co(II) matrices. Such small but uniform size NaBr crystallites with excellent dispersion in F–Co(II) reveals the high dispersity of the emulsion in scCO_2 . It is noted that Zielinski *et al.*¹³ showed micelle sizes in scCO_2 of about 4.0–7.2 nm. To conclude, water– scCO_2 is shown to be an excellent alternative solvent to acetic acid for the important Co(II) air-oxidation process. The generic concept of using H_2O – scCO_2 emulsions to bring species of different polarities into contact with excellent mass and heat transfers in sustaining a fast catalytic reaction is now, for the first time, demonstrated. We believe that this novel nano-reactor system could be utilized for a wide range of oxidations.

Notes and references

[†] Fluoros species synthesis, properties and characterisations: F–Co was synthesised via addition of 4 mmol nonadecafluorodecanoic acid (NDFDA) into 5 ml of a freshly prepared solution of CoCO_3 (4 mmol) in methanol. The mixture was kept at 40 °C and continually stirred. 10 ml diethyl ether was then added to stabilise the fluorinated Co(II) species formed. As a result, most of the solid was dissolved after 16 h. After filtering, a pink solid was obtained following removal of solvent. This solid was dissolved in diethyl ether and passed through a column of silica for purification. Chemical microanalysis and atomic absorption showed the dried blue compound (pink when hydrated) to be $(\text{CF}_3(\text{CF}_2)_8\text{CO}_2)_{1.95}\text{Co}$. IR (Nujol) showed a strong C=O absorption at 1657 cm^{-1} (sharp) as in the carboxylic anion form while the NDFDA has weaker absorption at 1717 (broad) in the acid form. This fluoros Co salt was able to form a cloudy colloidal suspension in water with stirring. Its melting point was determined to be 138–139 °C. The analogues of fluoros tagged Mg (mp 152–154 °C) and K (mp 205–207 °C) were also synthesised.

- A. K. Suresh, *Ind. Eng. Chem. Res.*, 2000, **39**, 3958.
- (a) M. P. Czytko and G. K. Bub, *Ind. Eng. Chem. Prod. Res. Dev.*, 1981, **20**, 481; (b) W. Partenheimer, *Chem. Ind.*, 1990, **40**, 321.
- E. Sahle-Demessie, M. A. Gonzalez, J. Enriquez and Q. Zhao, *Ind. Eng. Chem. Res.*, 2000, **39**, 4858.
- S. A. Chavan, S. B. Halligudi, D. Srinivas and P. Ratnasmy, *J. Mol. Catal.*, 2000, **161**, 49.
- J. M. Desimone, E. E. Maury, Y. Z. Menecelglu, J. B. McClain, T. J. Romack and J. R. Combes, *Science*, 1994, **265**, 356.
- R. J. Klingler and J. W. Rathke, *J. Am. Chem. Soc.*, 1994, **116**, 4772.
- M. G. Hitzler and M. Poliakoff, *Chem. Commun.*, 1997, **17**, 1667.
- A. M. Steele, J. Zhu and S. C. Tsang, *Catal. Lett.*, 2000, **73**(1), 9.
- (a) K. P. Johnston, K. L. Harrison, M. J. Clarke, S. M. Howdle, M. P. Heitz, F. V. Bright, C. Carlier and T. W. Randolph, *Science*, 1996, **271**, 624; (b) D. E. Fremgen, E. S. Eugene, R. E. Gerald, R. J. Klingler and J. W. Rathke, *J. Supercrit. Fluid.*, 2001, **19**, 287.
- P. A. Psathas, E. A. Sander, M. Y. Lee, K. T. Lim and K. P. Johnston, *J. Dispersion Sci. Technol.*, 2002, **23**, 65.
- A maximum of 32.6 mmol toluene can be dissolved in ca. 111 ml scCO_2 at 150 bar at 120 °C according to GC analysis using trace benzene as a standard. Results are consistent with lit. solubility diagrams: K. M. Dooley and F. C. Knopf, *Ind. Eng. Chem. Res.*, 1987, **26**, 1910.
- R. Wiebe, *Chem. Rev.*, 1941, **29**, 475.
- R. G. Zielinski, S. R. Kline, E. W. Kaler and N. Rosov, *Langmuir*, 1997, **13**, 3934.