Catalysis Letters Vol. 106, Nos. 3–4, February 2006 (© 2006)
DOI: 10.1007/s10562-005-9618-0

A new oxidation catalyst system using fluorous cobalt(II) species in water-supercritical carbon dioxide (C–H free environment)

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Received 6 October 2005; accepted 1 November 2005

Stabilized water droplet dispersed in supercritical carbon dioxide fluid is demonstrated to be an excellent alternative solvent system to acetic acid for air oxidation of a number of alkyl aromatic hydrocarbons using Co(II) species at mild conditions.

KEY WORDS: supercritical carbon dioxide; oxidation; micro-emlusion; alkyl aromatic hydrocarbons; catalysis; selectivity.

1. Introduction

Partial catalytic oxidation of alkyl aromatic hydrocarbons with air involving C–H bond activation is a key step for the production of oxygenated intermediates [1]. The challenges of further developing this process include identification of active but also extremely selective catalyst system for the hydrocarbon oxidation at mild conditions whereby catalytic C–H bond activation should be ultra-specific to the particular location of the hydrocarbon (avoidance of unselective C–H and C–C attacks to other part of the hydrocarbon, catalyst ligand(s) or solvent molecule). In addition, rapid & ease of isolation of product from catalyst and safe operation of the highly exothermic oxidation reactions are required. As a result, only limited catalytic systems can meet some of these criteria. At present, the primary industrial method employs pressurized air in *acetic acid–water mixture* using homogeneous cobalt species in the presence of promoter(s) (Mn ions and/or bromide) [2]. During the oxidation conditions, the active Co(III) species is responsible for the hydrocarbon activation. It has been suggested that acetic acid provides a polar medium for the interaction of ionic cobalt salt/promoter (hydrophilic) with hydrocarbons (hydrophobic in nature) in air, and to facilitate electron transfer between Co(II) and Co(III) with acetate/acetic during catalysis [3]. It is noted that oxidation of acetic acid is kinetically more sluggish than the hydrocarbons. However, there is still a significant solvent oxidation to carbon oxides [3]. In addition, the low energy efficiency, use of corrosive and toxic acetic acid, product over-oxidation, difficulty in solvent and catalyst recovery, and explosion hazards associated with the solvent and dioxygen (with reported explosions) are also obvious [4]. With increasingly demanding environmental legislation, public and corporate pressure, and the disadvantages of this technology, the process is becoming less economically competitive [5].

Supercritical carbon dioxide ($scCO_2$) is an ecologically benign solvent [6] being non-toxic, chemically inert, and non-combustible with no C–H or C–C structure. $scCO_2$ also has excellent mass transfer and is readily separated from product/catalyst, however, there is limited work concerning its use for catalytic partial oxidation [7]. This is partly due to incompatible polarity of the catalytic species, products or by-products (i.e. water produced from oxidation could lead to blockage of pores in heterogeneous catalyst [7] in $scCO_2$ attenuating the mass transfers needed for catalysis. On the other hand, there have been advances toward the formation of aqueous micro-emulsions using a variety of different fluorinated surfactants. Some fluorinated species can modify the interfacial tension of the $scCO_2$ forming a stable micro-emulsion [8]. Recent reports show that these systems allow good dispersion of ionic or polar species [9] and can carry water-soluble catalysts [10] or precursors [11]. Our preliminary work also shows that the use of a simple cobalt(II) fluorinated acetate, $[CF_3(CF_2)_8CO_2]_2Co$ (F-Co(II)) in water–$scCO_2$ can selectively oxidize the primary α-carbon atom on phenyl ring to carboxylic group. (In toluene oxidation, 98% conversion and 99% selectivity to benzoic acid with an extremely high turnover frequency (TOF $= 6.19 \times 10^{-3}\ s^{-1}$), at 120 °C) [12]. However, the roles of this new fluorinated carboxylic salt with respect to water, and $scCO_2$ and its catalytic effect on other alkylaromatic molecules of different structures were not clear. Here, we present evidence, which suggests that the working state of the catalysis is the aqueous fine micro-emulsion in $scCO_2$. This allows extremely well dispersion of the water droplets carrying soluble Co(II) and NaBr species in $scCO_2$–water for the catalytic oxidations. We also report that this catalyst system can

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equally catalyze the selective oxidation of secondary α-carbon atoms on phenyl ring to oxygenates (aromatic alcohols and acetones) without inducing much fragmentation.

2. Experimental

Experiments were carried out using a stainless-steel autoclave of 160 mL (with a Teflon cup insert rendering the void ca. 111 mL) equipped with a stirrer. The autoclave was connected to a GC for monitoring reaction mixtures intermittently. High boiling products were analyzed quantitatively using HPLC. Cobalt(II) fluorinated acetate $[CF_3(CF_2)_8CO_2]_2Co$ (containing stable C–C and C–F but no C–H structures) was herein synthesized [12]. The Co catalyst (0.25 mmol) and H_2O (0.10 mL, DI) with or without promoter were typically added to the autoclave that hosted a small container holding 2.0 mL of an alkyl aromatic hydrocarbon i.e. toluene (18.8 mmol) in order to avoid their direct reaction. The autoclave was charged with 10 bar O_2 and CO_2 pumped into the autoclave. The amount of hydrocarbon used was readily soluble.

3. Results and discussion

Systematic evaluation of important parameters in the aerial oxidation of toluene reaction from a number of catalytic systems is presented in table 1. First, the well-known homogeneous catalyst system of Co(II) acetate/NaBr, for toluene oxidation in acetic acid, is poorly active and unselective in $scCO_2$–water (entry 1). Adding surfactant ($C_{12}H_{25}(OCH_2CH_2)_5OH$) is found ineffective in enhancing the conversion and selectivity (entry 2). Our synthesized fluorous Co(II) is clearly extremely active (>98%) and selective (>99%) for the toluene oxidation to benzoic acid in $scCO_2$–water (entries 3 and 4). Modification of organometallic complexes with fluorinated tails to render a complex soluble in $scCO_2$ is well documented. However, the possibility of the fluorous Co(II) as a homogeneous catalyst in $scCO_2$ is eliminated because the dehydrated $[CF_3(CF_2)_8CO_2]_2Co$ *in the absence of water* (entry 5) is ineffective. Our result also indicates that fluorous Co(II) as a catalyst is far more effective than the use of individual components (NDFDA acid and Co(II) acetate) with regards to yields (entry 3 versus entry 7). This suggests chelation using the fluorous head group in acid form and re-dispersion of Co(II) to accessible location from non-fluorous aqueous Co(II) acetate to $scCO_2$ may not readily occur. It is noted that the presence of water (entry 3 versus entry 5), $scCO_2$ (entry 3 versus entry 8) and bromide (entries 3, 4 versus entry 6) are of importance. Table 2 shows that the fluorous cobalt(II)/NaBr catalyst in water–$scCO_2$ (with oxygen) catalyzes oxidation of other aromatic hydrocarbons. The catalyst system is also found to be effective for the oxidation of xylene to terephthalic acid acid at a high yield. This time, secondary α-carbon atoms attaching on phenyl rings including ethylbenzene and methyl-anthracene are also investigated. It is very interesting to note that the C–H activation of these secondary α-carbon(s) gives exclusively the corresponding oxygenates (aromatic alcohols and acetones) or alkenes at good conversions. This is clearly in contrast to typical homogenous catalyst, which induces $\alpha-\beta$ carbon cleavages of the high alkylaromatic hydrocarbons at comparable conversions (i.e. forming phenol, methanol & formic acid, etc.) [13]. Our rate analysis shows a zero-order with respect to oxygen concentration, first-order with respect to hydrocarbons. The isotope studies, k_{C-H}/k_{C-D} (not shown) are also consistent with the traditional auto-oxidation mechanism. Therefore, it is believed that the Co(III) species initialize activation of the more labile C–H bonds in the alkyl substitution of the aromatic hydrocarbons releasing radicals to mobile phase ($scCO_2$ in this case) for subsequent auto-oxidation as the same manner as the homogeneous Co system. However, it is believed that the hydrophobic nature of the partial oxidized products (more soluble in $scCO_2$ than water) would significantly reduce their contact time with the hydrophilic Co(III) species (catalyst restricted in the micelles) hence accounting for the total absence of over-oxidations in this new solvent. In addition, it is apparent that our novel catalyst is effective for oxidation of these bulky

Table 1
Toluene (18.8 mmol) oxidation in 0.1 mL H_2O, 150 bar CO_2, 10 bar O_2 over 0.25 mmol Co(II) and 0.5 mmol promoter

Entry	Reaction medium	Catalyst	Promoter	Temp. (°C)	Toluene Conv. (%)	Select. to Benzoic acid (%)
1	$scCO_2$	$Co(OAc)_2$	NaBr	120	0.1	0
2	$scCO_2$	$Co(OAc)_2$, surfactant	NaBr	120	0.5	6.7
3	$scCO_2$	F-Co(II)[a]	NaBr	120	89.2	99.1
4	$scCO_2$	F-Co(II)	HBr	120	95.5	99.9
5	$scCO_2$	dehydrated F-Co(II)	NaBr	140	14.2	91.2
6	$scCO_2$	F-Co(II)	Nil	140	6.0	68.8
7	$scCO_2$	$Co(OAc)_2$, NDFDA[b]	NaBr	140	5.7	66.5
8	N_2	F-Co(II)	NaBr	120	3. 9	92.1

[a]F-Co(II) represents $[CF_3(CF_2)_8COO]_2Co(II) \cdot nH_2O$.
[b]NDFDA represents 0.5 mmol nonadecafluorodecanoic acid added.

Table 2
Partial oxidation of various alkyl aromatic hydrocarbons in 0.1 mL H_2O, 150 bar $scCO_2$ (10 bar O_2) at 120 °C for 24 h

Substrate (mmol)	Catalyst	Conv. (%)	Select. (%)
Toluene (18.8)	F-Co(II)/NaBr	98.1	99.9 (benzoic acid)
P-xylene (8.17)	F-Co(II)/NaBr/ $Mn(OAc)_4$	90.3	89.1 (terephthalic acid)
Ethylbenzene (8.2)	F-Co(II)/NaBr	49.2	83.7 (acetophenone); 16.3 (sec-phenylethyl alcohol)
9,10-dihydroanthracene (1.1)	F-Co(II)/NaBr	99.2	67.6 (anthracene); 32.4 (anthraquinone)
2-methyl anthracene (0.5)	F-Co(II)/NaBr	62.4	76.3 (2-methyl-anthraquinone); 23.7 (2-methyl-anthrone)

alkyl aromatics in $scCO_2$. These non-polar bulky hydrocarbons display a rather low solubility in acetic acid (one of the current and key industrial problems), which limits wide applications. In contrast, they have a considerable solubility in $scCO_2$ phase [6]. Visual inspection through sapphire windows revealed that our dehydrated fluorous Co acetate remained *insoluble* under the reaction conditions. Thus, interactions of the fluorinated tails of the $[CF_3(CF_2)_8CO_2]_2Co$ with the $scCO_2$ are apparently unable to over-ride the stronger ionic interactions within the solid in the absence of water. However, adding only a small quantity of water (400 μL H_2O) to the same F-Co(II)/NaBr mixture renders them totally soluble in $scCO_2$ forming a transparent fluid with no phase boundary observed. Detailed post-mortem analysis of the catalyst by a rapid de-pressurization (F-Co(II)/NaBr/400 μL H_2O) revealed a solid foam. The volume of the foam is many times larger than the powder initially added (see figure 1). This suggests the penetration of the $scCO_2$ into the solid. TEM micrographs (figure 2) indicate uniform size NaBr crystallites of about 3 ± 1 nm dispersed extremely well in non-crystalline fluorous Co(II) matrices. EDAX mapping of the material using nano-probe (27.5 nm) gives a constant atomic Br/Co ratio of 0.16 *pm* 0.03 (calibrated against $CoBr_2$) indicative of well-dispersity. It is believed that such small size NaBr crystals with intimate contact with F-Co(II) species in an extremely well dispersity state could not be obtained from direct crystallization (original NaBr in micron size) without the invoke of fine micro-emulsion formation [8]. Note that Zielinski *et al.* [14] characterized a micro-emulsion in $scCO_2$, which showed the micelle diameter in the range of 4.0–7.2 nm. Our concentration of the F-Co(II)/H_2O is ~0.7 wt%, which is also comparable to other reported fluorous surfactant concentrations of 0.1–0.5 wt% in forming micelles in $scCO_2$ [10]. Thus, the working state of the catalyst is attributed to a tiny but plenty of aqueous micro-emulsion as *nano-reactors* which contain Co(II) and NaBr for the efficient interfacial catalysis with hydrocarbons pre-dissolved in $scCO_2$.

Figure 1. A solid foam formed from the fluorous catalyst mixture after an exposure to $scCO_2$–H_2O; fluorous catalyst before (left) and after (right) the $scCO_2$-H_2O treatment.

4. Conclusion

To conclude, the water–$scCO_2$ is shown to be an excellent alternative solvent to acetic acid for the important Co(II) air-oxidation process. The organic-free ligand/stabilizer and solvent system containing no C–H structure with an excellent dispersion of Co(II)/NaBr species are well suited for ultra-selective oxidation reactions. In addition, the generic concept of using the H_2O–$scCO_2$ micro-emulsion to bring species of a very different polarity into contact with excellent mass & heat transfers in sustaining a fast catalytic reaction could be utilized for a wide range of oxidations. H_2O–$scCO_2$ as a solvent will exhibit real advantages by providing a 'green' process with safer operation, easier separation and purification, high catalytic activity with selectivity and with no loss of solvent by oxidation.

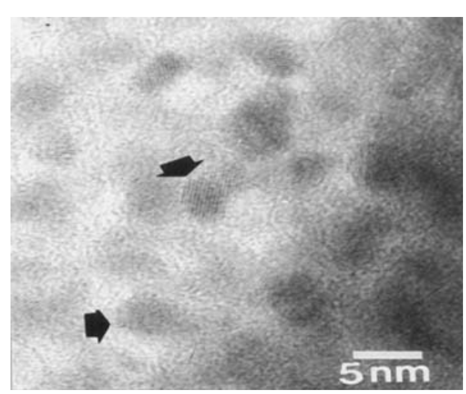

Figure 2. TEM micrograph showing 3 ± 1 nm NaBr crystallites dispersed in non-crystallined matrices: carbon, fluorine, cobalt and oxygen (EDAX). Lattice fringes of ca. 3.0 ± 0.2Å separation corresponding to (200) of NaBr crystallographic planes.

Acknowledgements

We are grateful to the EPSRC (GR/S41609) of UK and EU (GSRD-CT-2001-00519) for the partial support for this work.

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