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Selective oxidation of cyclohexane in supercritical carbon dioxide

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A feasibility study into the novel concept of using molecular oxygen to carry out one-step catalytic oxidation of cyclohexane to adipic acid in supercritical carbon dioxide over two types of catalysts, namely $Co^{2+}/Mn^{2+}/NaBr$ and Ag polyoxometallate, the silver decamolybdodivanadophosphate ($Ag_5PMo_{10}V_2O_{40}$) was carried out. Poor activity and selectivity towards adipic acid were initially noted over the aqueous micellar $Co^{2+}/Mn^{2+}/NaBr$ catalyst for the cyclohexane oxidation in supercritical carbon dioxide while under comparable conditions, the same catalyst gave a high activity for alkylaromatics oxidation to corresponding acids. It was later found that the adipic acid, being the extremely polar oxidised products, was virtually insoluble in the supercritical phase, which was rapidly degraded to carbon oxides after its prolonged contact with catalyst and O_2. Thus, the one-step cyclohexane oxidation to adipic acid with good selectivity can only be achieved by modifying the solvent with acetic acid or methanol, which enabled isolation of the acid from further oxidation. On the other hand, $Ag_5PMo_{10}V_2O_{40}$, in methanol modified supercritical carbon dioxide gave an impressive selectivity for cyclohexane conversion to other oxygenates.

KEY WORDS: supercritical carbon dioxide; oxidation; microemulsion; cyclohexane; heteropoly-acids; silver ion; catalysis; selectivity.

1. Introduction

Selective oxidation of alkanes to oxygenated products represents one of the most challenging chemical problems, in addition to being of great practical importance because of the fact that oxidation reactions are widely used in the chemical industry to manufacture both commodity and specialty products. Numerous oxidation processes have recently been receiving considerable attention especially those endeavouring to create greener chemical syntheses. For example, oxidation of cyclohexane is a major industrial process of importance for making adipic acid, which is extensively used in the man-made fibre industry for manufacturing nylon 6,6 plasticizers and synthetic lubricants. The conversion of cyclohexane, in first step, is necessary to keep only at 3–6% in acetic acid as solvent using a small quantity of $Co^{2+}/Mn^{2+}/Br^-$ as catalyst in at lower temperature regime (<120 °C) in order to maintain ~80% selectivity to cyclohexone and cyclohexanol (non-aromatic stabilisation oxygenates containing remaining C–H bonds are more susceptible for further oxidations leading to degradation of selectivity at higher conversion). The use of nitric acid as milder oxidant for the subsequent oxidation of cyclohexone/cyclohexanol to adipic acid in second step results in almost total oxidation of the other lower acids. Thus, this step leads to a substantial amount of carbon loss and a large amount of undesirable NO_x, which are environmentally critical compounds. Adipic acid is then recovered from the solution *via*crystallisation at 30–70 °C and the mother liquors are recycled although a fraction is drained to avoid accumulation of other gultaric and succinic acids. As a result, the associated problems arisen from the uses of acetic acid and nitric acid in this two-step process include the large amount of cyclohexane recycled (energy inefficient), the large amount of base necessary to neutralise the unselective acid products, the difficulties in separating and utilising the products obtained, the use of toxic and corrosive solvents that generates vapour and NO_x problems and discharge problems, etc. Therefore, this industrial oxidation is now regarded as a poor process with regards to environmental impact, energy, and raw material consumption which reveal the technical, economic and environmental problems in the C–H functionalisation of alkanes to oxygenates currently facing industry.

As a result, alternative synthetic routes have been developed for one-step oxidation of cyclohexane with either alkyl hydroperoxides or dioxygen in liquid phase [1–4]. Noticeably, Thomas et al have recently demonstrated a smart approach using a single site designed framework-containing Fe^{III}AlPO-31 catalyst which can give 65% selectivity towards adipic acid under aerial oxidation conditions [4].

On the other hand, supercritical carbon dioxide ($scCO_2$) is considered as an ecologically benign solvent

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for many catalytic reactions being non-toxic, chemically inert, and non-combustible (excellent for oxidation) with no C–H or C–C structure. $scCO_2$ also has excellent mass transport properties and is readily separated from product/catalyst via simple transfer and depressurisation. It may also offer the conversion of a traditional batch process to industrially more desirable continuous process. Thus, the main *aim* of the research described in this short paper was to undertake a feasibility study to develop a novel, cleaner one-step process for the selective catalytic oxidation of cyclohexane to oxygenated products, preferably to adipic acid at mild conditions in the supercritical CO_2. Concerning choice of the catalysts for this work it is noted that there were only few solid catalysts revealed in the literature to be both active and selective for oxidation of organic molecules using molecular oxygen without any use of sacrificial reagent(s). Thus, two types of well-studied catalyst systems, namely radical catalyst, Mn^{2+}/Co^{2+} [5–7] and non-radical Ag polyoxometallate catalyst [8], previously known to be both active and selective in molecular oxygen were therefore briefly studied.

2. Establishment of reaction and analytical set-ups

A schematic diagram of the high-pressure rig utilised in the experiments is shown:

A 300 mL Parr Series Mini batch reactor (316 stainless steel and equipped with a magnetic driver, by which the stirrer shaft could be driven) coupled with pipework to create supercritical testing conditions was purposely constructed for this work. The maximum working pressure of our setup was of about 250 bar at a maximum temperature of 350 °C. Suitable rupture discs were installed in the autoclave and in the pipelines, which could guarantee the safe operations since the burst of these facile discs could release pressure just above the threshold before a dangerous pressure was reached. At the end of a run, the products were collected by slowly releasing the mixture into a two-stage trap once the reactor had been cooled in a dry ice-acetone mixture (−75 °C). The double traps contained solvents (usually dichloromethane in this study unless otherwise specified), which were kept in another dry ice-acetone mixture. The residue in autoclave was also extracted twice with methanol at 85 °C (superheated methanol). Then, all of the solvents were then combined. The cyclohexane and partial oxygenated products analysis were carried out by means of a Agilent GC/MS system equipped with a HP-5MS (0.25 mm × 30 m × 0.25 μm) capillary column. Although no internal standard was used throughout the study as it was hard to identify a stable internal standard for this catalytic oxidation reaction, an accurate quantity of toluene was added as an external standard for the product quantification. Thus, the amount of cyclohexane consumed and the formation of oxygenates products were quantitatively analysed by the GC/MS. An important point was that esterification must be conducted prior GC-MS analysis for the high boiling oxygenates and acid products. The total % conversion of cyclohexane and the total % conversion of cyclohexane to partial oxygenated products were determined with respect to the known amount of toluene added externally. Thus, the difference in the total cyclohexane conversion and the conversion of oxygenates (discrepancy in carbon balance) was attributed to the formation of carbon oxides due to total cyclohexane oxidation. Also, according to the analysis above there was no evidence that CO_2, methanol or acetic acid was involved for the product production.

2.1. $Co^{2+}/Mn^{2+}/Br^-$ *system*

It has previously reported that toluene can be oxidised to benzoic acid at high yield using aqueous micellar catalyst system (ME) in $scCO_2$ [5] whereby the micelles containing water-soluble redox metal ions (cobalt(II) acetate, 99.995% and manganese(II) acetate, 98% from Aldrich) together with Br^- as an radical initiator maintain an excellent contact with the hydrocarbon pre-dissolved in the fluid for rapid interfacial catalysis. Before the investigation of cyclohexane oxidation, other alkylaromatics were carried out for comparison. Table 1 summarises that the catalyst mixture of Co(II)/Mn(II) (1:1 molar ratio) with NaBr in the water-$scCO_2$ microemulsion (with oxygen) catalyzed oxidation of a range of aromatic hydrocarbons [7]. The catalyst system was also found to be effective for the oxidation of xylene to terephthalic acid at a high yield. Again,

Table 1

A summary of optimized partial oxidation of various alkyl aromatic hydrocarbons [7] as compared with cyclohexane in 0.1 mL H_2O, 150 bar $scCO_2$ (10 bar O_2) at 120 °C for 24 h

Substrate (mmoL)	Catalyst	Conversion/%	Selectivity/%
Toluene (18.8)	Co(II)/NaBr	98.1	99.9 (benzoic acid)
P-xylene (8.17)	Co(II)/Mn(II)/NaBr	90.3	89.1 (terephthalic acid)
Ethylbenzene (8.2)	Co(II)/NaBr	49.2	83.7 (acetophenone); 16.3 (sec-phenylethyl alcohol)
9,10-dihydroanthracene (1.1)	Co(II)/NaBr	99.2	67.6 (anthracene); 32.4 (anthraquinone)
2-methyl anthracene (0.5)	Co(II)/NaBr	62.4	76.3 (2-methyl-anthraquinone); 23.7 (2-methyl-anthrone)
Cyclohexane (9.3)	Co(II)/Mn(II)/NaBr	Trace	Trace

0.2 mmoL NaBr; 0.25 mmoL anionic fluorinated surfactant species, $[CF_3(CF_2)_8COO]_2^-$ were used.

selective oxidations of secondary α–carbon atoms attaching to phenyl rings such as ethylbenzene and methyl-anthracene were shown. However, when cyclohexane was studied over the same micelle catalyst system in $scCO_2$, we found virtually no reaction. The difference in reactivity can be rationalized by considering the homolytic bond cleavage of the substrates where the C–H bond in cyclohexane is much stronger than those in alkylaromatic compounds.

As a result, higher temperatures (155–215 °C) were applied and the results are summarized in table 2. It is interesting to find that Co^{2+} in water-CO_2 could then activate cyclohexane in $scCO_2/O_2$ mixture with a high conversion at above 155 °C, suggesting a higher temperature is indeed required to overcome the higher activation barrier of the cycloalkane C–H (cyclohexane) than the aromatic stabilized C–H (toluene). However, as seen from the table 2, a very poor selectivity towards oxygenates was still encountered with carbon oxides as the main products. Attempts to enhance the selectivity towards adipic acid including the use of higher cyclohexane quantity, lower oxygen concentration, shorter reaction time, and slightly lower temperatures did not seem to enhance the selectivity in a significant way (not shown). This poor selectivity of the catalyst is attributed to the over oxidation of any partial oxidized intermediate products to carbon oxides. Solubility measurements indicated that the organic acid products from oxidations of the alkylaromatic compounds were fairly soluble in carbon dioxide (i.e. 30 mmoL benzoic acid was dissolved in 120 mL $scCO_2$ at 120 °C) but the adipic acid (extremely polar) was virtually insoluble in carbon dioxide. Thus, one would imagine that adipic acid, once formed, would not enter into the bulk supercritical fluid phase. It is therefore envisaged that the polar oxidised species including the adipic acid formed from the cyclohexane oxidation might have been retained within the aqueous micellar catalyst leading to unavoidable over-oxidation by a prolong contact with the catalyst to carbon oxides. Thus, a new strategy would be required to quickly extract any polar partial oxidised product from the oxidation catalyst in order to preserve them from further degradation from the aqueous based catalyst species. As a result, attempts to modify the $scCO_2$ solvency by either blending the carbon dioxide with polar acetic acid or methanol were carried out since both acetic acid and methanol showed a good solubility for adipic acid. In the acetic acid blended supercritical fluid, it was observed from the entry 2 in table 3 that a significantly higher conversion of cyclohexane to acids was indeed achieved as compared to those data without the acetic acid incorporation using the Br^- as the radical initiator. Also, a very clear reactivity difference can be distinguished using stable dialkylnitroxyl radical initiator, such as the archetypal TEMPO [9], and *N*-hydroxyphthalimide (NHPI). The reactivity observed was rationalized by considering the lower bond dissociation energies (BDEs) of the N-hydroxy precursors for generating radicals than the bromide ions for the cyclohexane oxidation. It was very interesting to note that by using the diacylnitroxyl radical initiator which was generated in situ from the corresponding *N*-hydroxy compound [10], the protagonist, NHPI clearly catalyzed the one-step oxidation of cyclohexane to acids (predominantly the adipic acid) in $scCO_2$-acetic acid mixture. It is particularly noted that NHPI is only soluble in acetic acid but not in water. Without the acetic acid modification to the $scCO_2$ (see entry 1 of table 3) almost no conversion was obtained. The presence of NHPI may therefore increase the rate of chain propagation and/or decrease the rate of chain termination. However, the optimum selectivity to oxygenates under this radical catalyst system was only 67.4% (entry 4) though higher than those of Fe^{III}AlPO-31 in similar conditions [4] which is still low for any viable commercial process. As a result, $Ag_5PMo_{10}V_2O_{40}$ as a new type of non-radical oxidation catalyst was then briefly studied in the modified supercritical carbon dioxide fluid.

2.2. $Ag_5PMo_{10}V_2O_{40}$ *system*

It has recently been reported that $Ag_5PMo_{10}V_2O_{40}$ prepared by metathesis precipitation of $Na_5PMo_{10}V_2O_{40}$ and $AgNO_3$ can catalyse O_2 sulfoxidation of 2-chloroethyl ethyl sulphide with ultra-high selectivity in a non-radical manner [8]. Structural characterisations indicated that Ag(I) bonded directly to both bridging and terminal oxygens of the POM

Table 2
A summary of optimized partial oxidation of cyclohexane in micelle catalyst system (ME) in $scCO_2$ at high temperatures

Catalyst	T/°C	Reaction Time/h	C_6H_{12} Conv./%	Conv. to partial oxygenated products/%	$S_{-KA\ oil}$/%	$S_{-diacids}$/%	$S_{-1,1\text{-}dmc}$/%
Co(II)/Mn(II)/NaBr	215	6	16	1.51	33	52	0
Co(II)/Mn(II)/NaBr	180	6	10	0.98	30	60	0
Co(II)/Mn(II)/NaBr	155	6	5	trace	–	–	–
Co(II)/Mn(II)/NaBr	155	24	7	1.10	41	56	0

Pressure applied: 140 bar for all entries; 20 bar of O_2 was charged where molar ratio of $C_6H_{12}/O_2 = 1/1.32$, Catalyst: 0.325 mL of 0.384 M (with respect to each metal ions) solution used; 0.2 mmoL NaBr used; KA = (cyclohexanone + cyclohexanol); di-acids = (adipic + glutaric + succinic acid); 1,1-dmc = (1,1-dimethoxycyclohexane).

Table 3
A summary of conversions, product distributions and turnover frequencies obtained over 1.0% Co(II)/Mn(II) in acetic acid-modified $scCO_2$ with different radical initiators

Entry	Acetic acid/mL	Radical initiators [a]	Temperature/°C	C_6H_{12} Conv./%	Conv. to oxygenates/%	TOF/h^{-1} [b]	$S_{-KA\ oil}$/%	$S_{-diacids}$/%
1	0	NHPI 5.0%	155	0	0	0	0	0
2	7.5	NaBr 5.0%	155	16.5	4	1	Cyclohexanol (33.9%) Cyclohexanone (34.7%)	Succinic acid (9.7%); Glutaric acid (7.4%); Adipic acid (14.4%)
3	7.5	TEMPO 5.0%	155	17.8	5	2	Cyclohexanone (27.7%)	Succinic acid (12.8%); Glutaric acid (11.9%); Adipic acid (47.6%)
4	7.5	NHPI 5.0%	80	54.9	37	7	0	Succinic acid (1.8%); Glutaric acid (3.4%); Adipic acid (94.8%)

Cyclohexane (5 mL); O_2 (20 bar); total pressure (140 bar) and time (8 h), Catalyst: Co(II)/Mn(II) 1.0% with metal salts molar ratio of Co:Mn = 1:1; [a] molar percentage of metal ions/radical initiators added with respect to cyclohexane molar ratio $C_6H_{12}/O_2 = 1/1.32$ used; KA = (cyclohexanone + cyclohexanol); di-acids = (adipic + glutaric + succinic acid); [b] TOF = [(Total number of mole of oxygenates produced)/(Total number of mole of metal ion)]/hours.

units, rending them as reactive forms of oxygen for hydrocarbon oxidations [8]. As a result, the $Ag_5PMo_{10}V_2O_{40}$ was prepared by our solid synthesis method using $H_5PMo_{10}V_2O_{40}$ and $AgNO_3$ [11,12]. Also, ca. 5 mL methanol was used to modify the $scCO_2$ for the cyclohexane oxidation (to extract the polar products to the bulk phase) over this catalyst. From table 4, the active and selective nature of the $Ag_5PMo_{10}V_2O_{40}$ catalyst can be clearly identified in this study. Here, we demonstrate that the $Ag_5PMo_{10}V_2O_{40}$ is very active and selective for the one-step cyclohexane oxidation in $scCO_2$/methanol mixture at 180 °C while using lower temperature (155 °C) results in low acid yield and higher temperature (215 °C) enhances subsequent oxidation. At the optimum temperature of 180 °C, the reaction selectivity reached nearly 100% selectivity to oxygenates without producing significant combustion products. It is particularly noted that there was no reaction in the absence of catalyst or in the presence of $Na_5PMo_{10}V_2O_{40}$ under the same conditions. The product distribution over this non-radical catalyst system appeared to be different from those of Co^{2+}/Mn^{2+} system with a higher selectivity towards cyclohexanone, cyclohexanol and other acids. Clearly, there is a synergetic effect between the Ag(I) cationic centres and the redox oxygen centres. In order to appreciate the reactive oxygen centres from the $Ag_5PMo_{10}V_2O_{40}$, temperature programmed reduction (TPR) was studied as compared with the $Na_5PV_2Mo_{10}O_{40}$ (see figure 1). As seen from the figure, three reduction peaks corresponding at 200, 500 and 650 °C can be clearly seen from the $Ag_5PMo_{10}V_2O_{40}$. On the other hand, the sodium salt of the corresponding polyoxometallate showed no labile reduction peaks below 600 °C. It is attributed to the fact that the ionic nature of the $Na_5PMo_{10}V_2O_{40}$ does not allow facile reduction of the oxygens while the Ag form clearly enhances the redox properties of this structure as previously suggested in the literature [8]. As a result, this new preliminary work suggests that the one-step selective oxidation of cyclohexane at 10% conversion with 96% selectivity to oxygenates can be achieved over the $Ag_5PMo_{10}V_2O_{40}$ catalyst in the methanol modified $scCO_2$ solvent.

Table 4
A summary of optimized partial oxidation over $Ag_5PMo_{10}V_2O_{40}$ catalysts in $scCO_2$-methanol under various conditions

Catalyst	T/°C	Reaction Time/hr	C_6H_{12} Conv./%	Conv. to partial oxygenated products/%	$S_{-KA\ oil}$/%	$S_{-diacids}$/%	$S_{-1,1\text{-}dmc}$/%
0.1g$Ag_5PMo_{10}V_2O_{40}(CH_3OH)$	215	6	22.0	4.24	21	33	17
0.05g$Ag_5PMo_{10}V_2O_{40}(CH_3OH)$*	**180**	**2**	**10.0**	**9.60**	**28**	**40**	**19**
0.05g$Ag_5PMo_{10}V_2O_{40}(CH_3OH)$	155	2	0.4	0.35	54	12	32
0.05g$Na_5PMo_{10}V_2O_{40}(CH_3OH)$	180	2	0.0	0.00	0	0	0

Pressure applied: 140 bar for all entries, 20 bar of O_2 was charged where molar ratio of $C_6H_{12}/O_2 = 1/1.32$, CH_3OH = adding 5 mL methanol
*Selectivity: KA= (19.3% cyclohexanone + 8.5%cyclohexanol); di-acids = (18.7%adipic + 11.1%glutaric + 10.6% succinic acid); 1,1dmc = (18.9% 1,1 dimethoxycyclohexane).

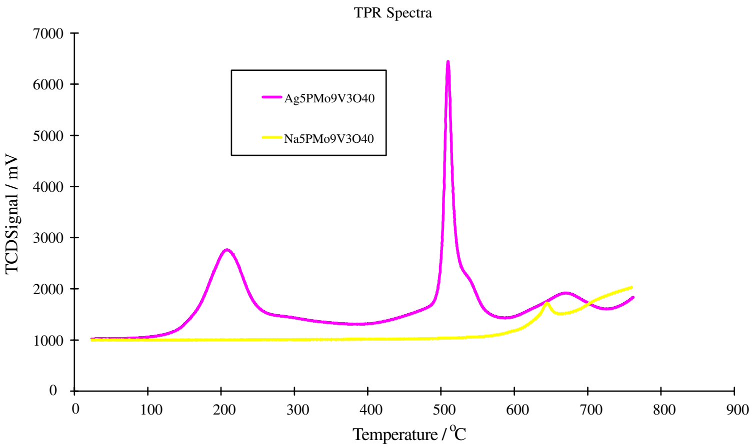

Figure 1. Temperature programmed reduction of $Ag_5PMo_{10}V_2O_{40}$ (0.022 g) showing the two characteristic labile reduction peaks as compared with the ionic nature $Na_5PMo_{10}V_2O_{40}$ (0.028 g) with no equivalent reduction peaks at the same ramping rate of 10 °C/min in a flowing stream of 20 mL/min 5% H_2/Ar

3. Conclusions

This preliminary study has elucidated some important fundamental aspects of oxidation of organic molecules in supercritical carbon dioxide/oxygen mixture at mild temperatures. The partial oxidised product(s) such as adipic acid (with chelating properties) from cyclohexane oxidation would have to be desorbed from the catalytic site readily otherwise a poor activity will be resulted. Thus, the poor solubility of the adipic acid (extremely polar) in $scCO_2$ renders the aqueous microemulsion catalyst system in $scCO_2$ non-feasible for the one-step oxidation of cyclohexane to adipic acid at high yield. On the other hand, it is demonstrated that a substantially higher yields towards adipic acid in one-step oxidation can be achieved by modifying the $scCO_2$ solvent with acetic acid or methanol which extracts the adipic acid or related polar intermediates from the catalytic production site. In addition, new and promising radical initiator, the NHPI and the $Ag_5PMo_{10}V_2O_{40}$ catalyst for ultraselective cyclohexane oxidation were identified. Thus, the findings make it possible to adopt future new approaches to the design of novel catalyst systems in environmental benign solvent, the supercritical carbon dioxide for the selective oxidation of organic molecules with appropriate catalyst/solvent modifier/initiator. This may lead to cleaner processes for making high value chemicals with important consequences for the creation of a sustainable chemical industry.

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