Highly selective oxidation of tetralin to 1-tetralone over mesoporous CrMCM-41 molecular sieve catalyst using supercritical carbon dioxide†‡

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Selective oxidation of tetralin by molecular oxygen over mesoporous CrMCM-41 molecular sieve catalyst using supercritical carbon dioxide ($scCO_2$) solvent has been investigated. CrMCM-41 catalyst gave high selectivity (96.2%) and good yield (63.4%) of 1-tetralone. The presence of $scCO_2$ medium improves 1-tetralone selectivity and suppresses leaching of chromium from the CrMCM-41. The activity over recycled CrMCM-41 remains nearly the same under the present experimental conditions. The effect of the reaction parameters on CrMCM-41 was also studied in detail along with comparison of its catalytic activities with other mesoporous catalysts, *viz.* MnMCM-41, CoMCM-41, microporous CrAPO-5, CoMFI, and macroporous Cr/SiO_2 catalyst, respectively. In addition this catalytic system was also applied for the oxidation of other benzylic compounds such as indane, fluorene, acenaphthene and diphenylmethane.

Introduction

Tetralones are important intermediates in the production of many compounds, including sertraline, an antidepressant, naphthyl carbamate, an insecticide, and 18-methylnorethisterone, a contraceptive, respectively.[1] It is estimated that the worldwide market for tetralone as a pharmaceutical/agrochemical intermediate exceeds approximately €3 million per year.[2]

Tetralones have been produced by intramolecular condensation reactions using metallic reagents, such as aluminium chloride[3,4] which generate large volumes of metallic hydroxides as waste. These processes are also multi-step synthesis processes, so the overall yield of tetralone is very low.[4] A number of studies claiming one-step synthesis of tetralones have been proposed including those by intramolecular Friedel–Crafts reaction of 4-arylbutyric acids in the presence of Lewis acid catalysts,[5] alkylation–acylation of aromatics with γ-butyrolactone using supported heteropolyacids[6] and ionic hydrogenation of 1-naphthol by superacid.[7] However, the above processes use excess quantities of starting materials and require highly acidic catalysts. Hence these procedures are hardly compatible with environmental regulations. Recently, alkyl-substituted tetralone compounds have been synthesized from *p*-xylene, or other benzene derivatives with cyclic lactones using a molecular sieve based catalyst (*e.g.*, zeolite).[2] This new solid acid catalyst technology enables a substantially decreased production cost owing to reduction in the volume of wastes. Though zeolites have attracted strong attention as solid acid catalysts,[8] they present severe limitations due to their smaller pore size when larger molecules are involved, especially in liquid phase oxidation systems.[9]

Another well studied process for synthesis of 1-tetralone is the direct oxidation of tetralin. Numerous reports are available on oxidation of tetralin in the presence of oxidative catalysts.[10–17] From these investigations it is established that the primarily formed 1-tetralin hydroperoxide (THP) decomposes catalytically into a mixture of 1-tetralone and 1-tetralol. Selective transformation of THP is a vital issue to improve the yield of 1-tetralone. Since hydroperoxide is explosive, its complete decomposition is also essential. Therefore, many inorganic reagents such as chromium oxide, manganese dioxide, pyridinium dichromate, *etc.*, and/or metallic catalysts, *e.g.*, chromium, manganese, cobalt, copper, iron salt *etc.*, have been extensively studied.[10–12] However, these methods do not promote complete decomposition of THP. Additionally, these catalytic systems generate copious quantities of metal wastes, along with tedious work up, difficulties in separation/reusability of the catalyst *etc.* which makes them environmentally unsuitable.

Consequently, a large number of heterogeneous catalysts have been analyzed and proved to be effective for the selective oxidation of tetralin.[13–17] Usually heterogeneously catalyzed tetralin oxidations are performed in volatile and/or toxic organic solvents such as methanol, chlorobenzene, dichloromethane *etc.*, in combination with *tert*-butyl hydroperoxide solution (TBHP, 70 wt% in water) as an oxidant.[13–17] These catalytic systems are effective for the decomposition of THP. In addition, mesoporous CrMCM-41 molecular sieve catalyst has been found to be promising for the liquid phase oxidation of tetralin with 70 wt% TBHP oxidant.[15,16]

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† Note that the term "supercritical" in this paper is used for a reaction mixture exceeding the critical point of the solvent, despite several phases present.

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Although hydroperoxide is a satisfactory oxidant, its use along with toxic solvents during these processes is far from being environmentally benign.[18]

For developing a more environmental-friendly process for the synthesis of 1-tetralone, it is beneficial to use molecular oxygen/air and non-toxic solvents along with an effective catalytic system. A new "greener" approach which has attracted attention is the use of supercritical carbon dioxide ($scCO_2$) as solvent for various alcohol, alkene, and alkane oxidation reactions with a clean oxidant (molecular oxygen).[19] It has been reported that the presence of $scCO_2$ can improve yields, reaction rates and/or product selectivity in oxidation reactions.[20]

Here we report a simple one-step process for the synthesis of 1-tetralone by direct oxidation of tetralin over CrMCM-41 catalyst using $scCO_2$ with molecular oxygen.

Experimental

Catayst preparation

CrMCM-41 catalyst comprising 2.0 wt% chromium was prepared as described previously with slight modification in molar gel composition.[21] Synthesis and characterization are provided in the ESI.‡

Reaction procedure

Oxidation of tetralin was carried at 80 °C for 14 h in a stainless steel high pressure reactor equipped with a specially designed Teflon insert (Φi.d.: 38 mm and inner volume: 40 cm^3). In a typical experiment, 2 mmol tetralin and 40 mg CrMCM-41 were placed inside the reactor vessel. The reactor was flushed with 2 MPa CO_2 followed by 1.0 MPa O_2 (two times) and then heated to 80 °C. To start the reaction, the reactor was charged with 2 MPa O_2 from the O_2 cylinder followed by pumping CO_2 using JASCO SCF-Get CO_2 delivery pump to the desired pressure. Stirring was achieved by means of a magnetic stirrer, the motor of which was set at one-half max speed (approximately 360 rpm). The total pressure of reaction system was maintained by SCF-BPG/M (JASCO) back pressure regulator. After the reaction was over, the reactor was cooled in an ice-bath and the reactor slowly depressurized through a back pressure regulator.[22] The reaction products were collected by simple conventional filtration of the reaction mixtures through a Advantec filter paper. Finally, the catalyst was separated and calcined at 540 °C for 6 h. The regenerated catalyst was used for recycling experiments.

Visual observation of the phase behavior in $scCO_2$

A high-pressure view cell (JASCO; Model STR-458, internal volume 10 ml) was used to observe the phase behavior of tetralin in $scCO_2$. The cell is equipped with windows and connected to a temperature-controlled bath. A magnetic bar is used to mix the contents in the viewing cell. The phase behavior experiment was conducted in the range of 6 MPa to 16 MPa CO_2 pressure with 2 mmol of tetralin at 80 °C and 2 MPa oxygen pressure.

Product analysis

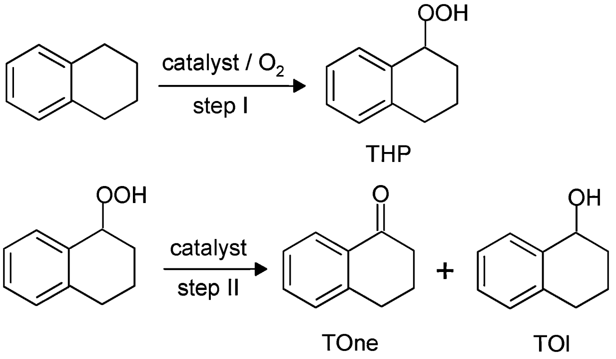
The reaction products were analyzed by capillary gas chromatography using a FID (Chromatograph: Varian CP 3800, column: HP-5, 30 m (length) × 0.32 mm (inner diameter) × 0.25 μm (film thickness). The identity of the products was first confirmed by using authenticated standards and their individual response factors were determined by using a suitable internal standard phenylacetonitrile by the calibration method. Additionally, the identity of the reaction products was also confirmed by using GC-MS (Varian CP 3800, 1200L Quadrupole MS/MS, column: HP-1 30 m (length) × 0.32 mm (inner diameter) × 0.25 μm (film thickness). The THP, TOne and TOl selectivity was also determined by ^1H NMR on Varian Unity INOVA-500.

Results and discussion

In case of tetralin oxidation, it is established in the literature[10–12] that the primarily formed 1-tetralin hydroperoxide (THP) (Scheme 1, Step I) decomposes in presence of the catalyst into a mixture of 1-tetralone (TOne) and 1-tetralol (TOl) (Scheme 1, Step II).

At first, we studied the effect of various reaction parameters, for example, CO_2 pressure, oxygen pressure, reaction temperature, and reaction time on the conversion of tetralin and the product selectivity over CrMCM-41 catalyst.

It is well-known that the properties of $scCO_2$ are sensitive to pressure. Therefore, the effect of CO_2 pressure on the conversion and the product selectivity for the oxidation of tetralin was investigated over CrMCM-41 at 80 °C for 14 h and the results are shown in Table 1. As can be seen from Table 1, CO_2 pressure dramatically influences the catalytic activity. In the absence of $scCO_2$ solvent (entry 1), the catalyst showed low conversion of approximately 41% as well as low selectivity of 1-tetralone (75%). Surprisingly, in the presence of $scCO_2$ the catalyst revealed complete decomposition of THP, while in the absence of $scCO_2$ it did not. High 1-tetralone selectivity was observed in the presence of CO_2. A similar observation was reported in the literature that chromium containing catalysts do promote more decomposition of THP in liquid phase oxidation of tetralin.[10,11] Furthermore, with increase in CO_2 pressure from 6 to 11 MPa, 1-tetralone selectivity increases (entries 2–7). However at the moment



Scheme 1 Reaction scheme of the oxidation of tetralin.

Table 1 The effect of CO_2 pressure on the oxidation of tetralin over CrMCM-41[a]

Entry	CO_2 pressure/MPa	Phases[b]	Conversion of tetralin[c] (%)	Selectivity[d] (%) THP	TOl	TOne	Yield of TOne[e] (%)
1	0	s/l	40.8	18.0	7.0	75.0	30.6
2	6	s/l/g	47.4	0.0	9.2	90.8	43.0
3	7	s/l/g	48.7	0.0	8.0	92.0	44.8
4	8	s/l/g	60.0	0.0	4.5	95.5	57.3
5	9	s/l/g	65.9	0.0	3.8	96.2	63.4
6	10	s/l/g	42.4	0.0	2.9	97.1	41.2
7	11	s/sc	20.5	0.0	1.6	98.4	20.2

[a] *Reaction conditions*: 2 mmol tetralin; m(CrMCM-41) = 40 mg; P_{O_2} = 2 MPa; T = 80 °C; t = 14 h. [b] s—solid phase; l—liquid phase; g—gas phase; sc—supercritical phase. [c] Conversion of tetralin analysed by GC using phenylacetonitrile as an internal standard (see ESI†). [d] Product selectivity analysed by GC and also determined by ^{1}H-NMR. Selectivity of other by-product was left out because it was less than 1%. [e] Yield of TOne = [(conversion of tetralin × selectivity of TOne)/100].

reason for the increase in selectivity of 1-tetralone is not understood.

As CO_2 pressure increases (entries 2 to 4), tetralin conversion increases and reaches a maximum at 9 MPa CO_2 pressure (entry 5). Under this liquid/gas (l/g) biphasic system, CO_2 allows substantial quantities of oxygen to solubilize, providing for high rate of reaction. Recent work in the literature[23] shows that one can achieve high gas solubility and hence high reaction rate in such a moderate pressure system. With further increase in CO_2 pressure from 9 to 11 MPa, conversion decreases from 65.9 to 20.5% (entries 5 to 7). This suggests that the drop in activity with increasing CO_2 pressure is due to the transformation of the two-phase reaction system to a one-phase reaction system (sc phase). Therefore, we think that at high CO_2 pressure the reaction system is diluted as a consequence there is less interaction between the reactant/intermediate and the catalyst leading to a decrease in reaction rate. Similar trend of decrease in activity and an increase in product selectivity has been observed in other oxidation reactions using heterogeneous catalysts in $scCO_2/O_2$ systems.[24] It is worth mentioning that in the range of CO_2 pressure from 6 to 11 MPa, undecomposed THP was negligible. This clearly indicates that CrMCM-41 catalyst is highly effective for the generation and decomposition of THP in the presence of CO_2 media. In addition, we obtained less than 1% other by-products, *viz*. 1,4-naphthoquinone under present reaction conditions, which could have been formed due to the further oxidation of 1-tetralone.[10,12]

We examined the oxygen pressure effect at 9 MPa CO_2 pressure at 80 °C for 14 h. At <0.5 MPa oxygen pressure, conversion was approximately 45%. Above 0.5 MPa oxygen pressure, conversion increases and reaches a maximum in the range of 1 to 1.5 MPa pressure. We did notice a drop in the total pressure of reaction system but with the present reaction setup, oxygen consumption cannot be precisely measured. Thus, assuming the stoichiometry of reaction, we used excess amount of oxygen (32 mmol) equivalent to the oxygen pressure, *i.e.* 2 MPa for all catalytic experiments.

Fig. 1 shows the effect of reaction temperature on conversion of tetralin over CrMCM-41 using $scCO_2$.

It can be seen from the figure that tetralin conversion increases linearly as the temperature increases from 50 to 80 °C. With further increase in reaction temperature above 80 °C, conversion does not increase. Therefore we made an attempt to study the kinetics of the reaction in batch mode. However, as expected from the kinetic data, the reaction system is complex and does not follow the Arrhenius equation. We will be looking into getting a deeper insight on the complex behavior of reaction system by high pressure *in situ* infrared spectroscopy (FT-IR). A high 1-tetralone selectivity was observed even at lower reaction temperature and which increased as the temperature increased. On the other hand, as the reaction temperature increases generation of 1-tetralol is suppressed. This indicates that high reaction temperature promotes selective decomposition of THP into 1-tetralone and additional oxidation of 1-tetralol into 1-tetralone. The latter observation was confirmed by carrying out a separate catalytic experiment on 1-tetralol oxidation using $scCO_2$ at different reaction temperatures (see also Table 3, entry 2).

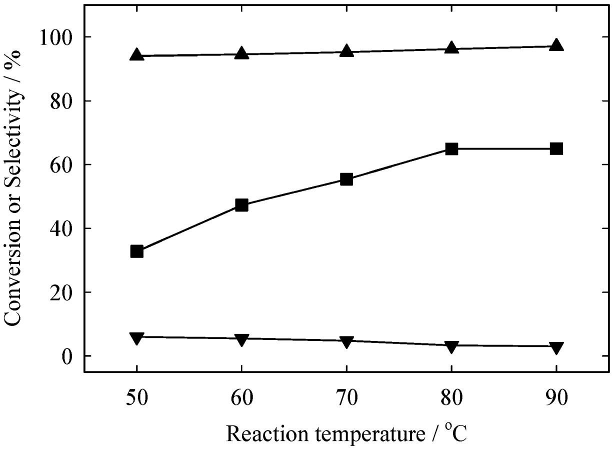


Fig. 1 Effect of reaction temperature on tetralin conversion and product selectivity over CrMCM-41: (■) conversion of tetralin, (▲) selectivity of 1-tetralone, (▼) selectivity of 1-tetralol. *Reaction conditions*: 2 mmol tetralin; m(CrMCM-41) = 40 mg; P_{O_2} = 2 MPa; P_{CO_2} = 9 MPa; t = 14 h.

The catalytic performance of CrMCM-41 as a function of reaction time was examined at 80 °C using $scCO_2$ and the results are shown in Fig. 2. At 4 h, we obtained only 32% tetralin conversion. The highest conversion of approximately 66% was obtained in the range of 14 to 20 h and with further increase in reaction time, conversion did not improve. The possible reason could be that after an initially fast reaction, the

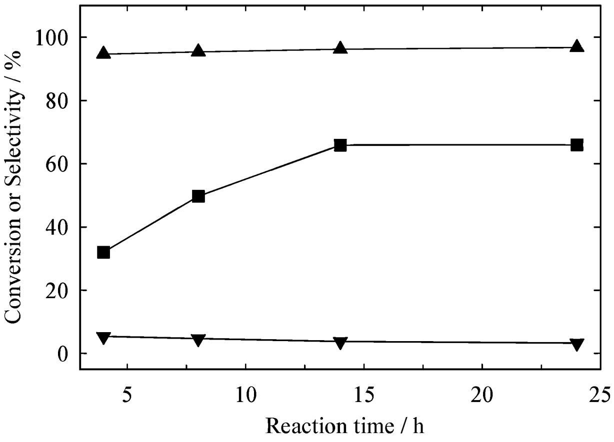


Fig. 2 Effect of reaction time on tetralin conversion and product selectivity over CrMCM-41: (■) conversion of tetralin, (▲) selectivity of 1-tetralone, (▼) selectivity of 1-tetralol. *Reaction conditions*: 2 mmol tetralin; *m*(CrMCM-41) = 40 mg; P_{O_2} = 2 MPa; P_{CO_2} = 9 MPa; *T* = 80 °C.

CO_2 within the pores of the catalyst may slow the extraction of the products out of the catalyst. This phenomenon may be more complex in porous catalysts under $scCO_2/O_2$ system.[25] In addition we found that the reaction was dependent on tetralin concentration. Also, a longer reaction period, for example 40 h, led to formation of approximately 2–3% by-products, mainly 1,4-naphthoquinone indicating that longer reaction time allows further oxidation of 1-tetralone. However, still over a wide range of reaction time from 4 to 24 h, 1-tetralone selectivity remains >95%.

The influence of various transition metal containing catalysts on the oxidation of tetralin by molecular oxygen using $scCO_2$ was studied and the results are shown in Table 2. It can be seen from entry 1 that in the absence of catalyst, conversion was only 9% with THP as a major product. CrMCM-41 catalyst showed good conversion (65.9%) and high 1-tetralone selectivity (96.2%) (entry 2).

Since we found that CrMCM-41 catalyst is highly effective for the decomposition of THP, we performed a recycling study on CrMCM-41. It can be seen from entry 3, that a slight decrease in conversion was observed as compared to entry 2, but, over recycled catalyst, conversion remains almost the same (entry 3 and 4). The analysis of chromium on recycled catalyst (entry 4) gave 1.7–1.8 wt% chromium as compared to fresh catalyst content of 2.0 wt% chromium. This shows that more than 85% chromium still remains even after the third run, indicating that under $scCO_2/O_2$ system there is no further leaching of chromium in the reaction mixture. We also analyzed the reaction solution obtained from recycled catalyst by ICP-AES, where no chromium was detected. On further recycling studies, carried out after the third run, conversion was found to be almost the same (≈60%) and no chromium leaching was detected. We suspect that the water generated as a by-product is responsible for the extraction of a small amount of loosely bound chromium in CrMCM-41 catalyst. Although minimal leaching occurred during the initial run in the subsequent runs no leaching was observed. Upon recycling 1-tetralone selectivity remains nearly the same (entry 3 and 4). For comparison, we carried out the liquid phase reaction in acetonitrile solvent over CrMCM-41 (entry 5) under similar reaction conditions, although conversion was low (36.3%), 1-tetralone selectivity was higher than in the $scCO_2$ solvent. Even at such low conversion, we noticed an approximately 20% decrease in conversion between the first and second run in acetonitrile solvent. This observation was further confirmed by chromium analysis where around 40% chromium leached out in the reaction mixture, indicating that organic solvent and/or water as by-product induces more leaching. A similar trend has often been observed using chromium containing silicate or aluminophosphate in liquid phase oxidations.[16,17,21,26] The reaction over macroporous Cr/SiO_2 catalyst (entry 6) showed higher conversion of approximately 70% and good 1-tetralone selectivity. However, upon recycling, this chromium catalyst (entry 7) showed a dramatic decrease in conversion from 70.2% to 30.3%. The decrease in conversion is again due to the leaching of chromium from silica support. This clearly indicates that the water generated (by-product) under the reaction conditions, extracts the loosely bound chromium species from the silica support. It is

Table 2 Results of the oxidation of tetralin by molecular oxygen over various transition metal containing catalysts using $scCO_2$[a]

Entry	Catalyst	Conversion of tetralin (%)	Selectivity (%) THP	TOl	TOne	Yield of TOne (%)
1[b]	Blank	9.0	78.0	2.4	19.6	1.8
2	CrMCM-41	65.9	0.0	3.8	96.2	63.4
3[c]	CrMCM-41	60.5	0.0	4.3	95.7	57.9
4[d]	CrMCM-41	59.6	0.0	5.8	94.2	56.1
5[e]	CrMCM-41	36.3	0.0	1.0	99.0	35.9
6	Cr/SiO_2	70.2	0.0	7.7	92.3	64.8
7[f]	Cr/SiO_2	30.3	0.0	4.1	95.9	29.0
8	CrAPO-5	24.6	0.0	10.0	90.0	22.1
9[g]	CrO_3	43.6	0.0	4.4	95.6	41.7
10	MnMCM-41	70.8	9.5	9.5	81.0	57.3
11	CoMCM-41	67.0	10.8	18.9	70.3	47.1
12	CoMFI	33.3	22.7	13.6	63.7	21.2

[a] *Reaction conditions*: 2 mmol tetralin; *m*(catalyst) = 40 mg; P_{O_2} = 2 MPa; P_{CO_2} = 9 MPa; *T* = 80 °C; *t* = 14 h. [b] Without catalyst. [c] 2nd run. [d] 3rd run. [e] *V*(acetonitrile solvent) = 3 ml. [f] 2nd run. [g] Homogeneous run (the amount of chromium was same as that of the amount of chromium (0.02 g Cr) in CrMCM-41.

known that the Cr/SiO_2 catalytic system is susceptible to leaching due the loosely bound chromium to silica. This implies that the CrMCM-41/scCO_2 reaction system suppresses the leaching of chromium, thereby recycled catalyst behaves as a true heterogeneous catalyst under the present experimental conditions.

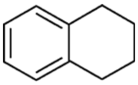
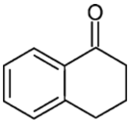
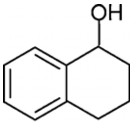
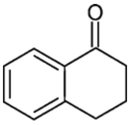
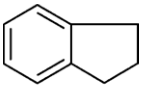
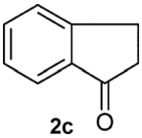
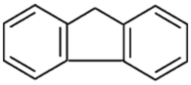
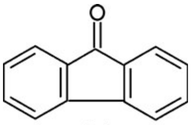
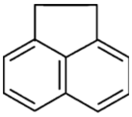
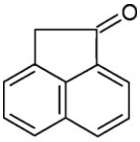
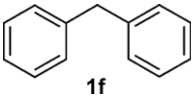
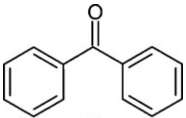
We also checked the activity over medium pore diameter chromium aluminophosphate (CrAPO-5) catalyst (pore diameter 0.73 nm). This chromium catalyst was effective for the decomposition of THP, thus giving good 1-tetralone selectivity, but showed low conversion (entry 8).

A homogeneous run was also carried out with CrO_3 using scCO_2 (entry 9). This chromium reagent gave approximately 44% conversion and high 1-tetralone selectivity, most interestingly no THP was detected.

Other mesoporous catalysts containing manganese and cobalt, *viz*., MnMCM-41 and CoMCM-41 (entries 10 and 11) showed comparable and/or little higher conversion than CrMCM-41, but 1-tetralone selectivities were low as compared to the CrMCM-41. Small pore cobalt microporous CoMFI catalyst (entry 12) showed low conversion compared to the mesoporous catalysts. The lower conversion could be due to the smaller pore diameter of MFI structure (pore diameter 0.55 nm) which restricts the diffusion of reactant/intermediate and products.[9] It is important to note here that MnMCM-41, CoMCM-41 and CoMFI catalysts do not promote complete decomposition of THP even in the presence of scCO_2. This observation is in the line of study on the tetralin oxidation using various metal acetates in acetic acid.[11]

Finally, we studied the selective oxidation of other benzylic compounds over CrMCM-41 using scCO_2 under similar experimental conditions. The results are summarized in Table 3. For comparison, oxidation of tetralin (**1a**) to 1-tetralone (**2a**) is also included in Table 3. It can be seen from entry 2 that the catalyst is highly active for the direct oxidation of corresponding benzylic alcohol *viz*., 1-tetralol (**1b**) and gave very good conversion of 80.1% with 1-tetralone (**2a**) selectivity of 95%. It was also highly active for indane (**1c**) oxidation and gave high 76.6% conversion and 1-indanone (**2c**) selectivity of 95% (entry 3). Fluorene (**1d**) was likewise oxidized with 52.4% conversion and 9-fluorenone (**2d**) selectivity of >99% (entry 4). When acenaphthene (**1e**)

Table 3 Selective oxidation of benzylic compounds over CrMCM-41 using scCO_2[a]

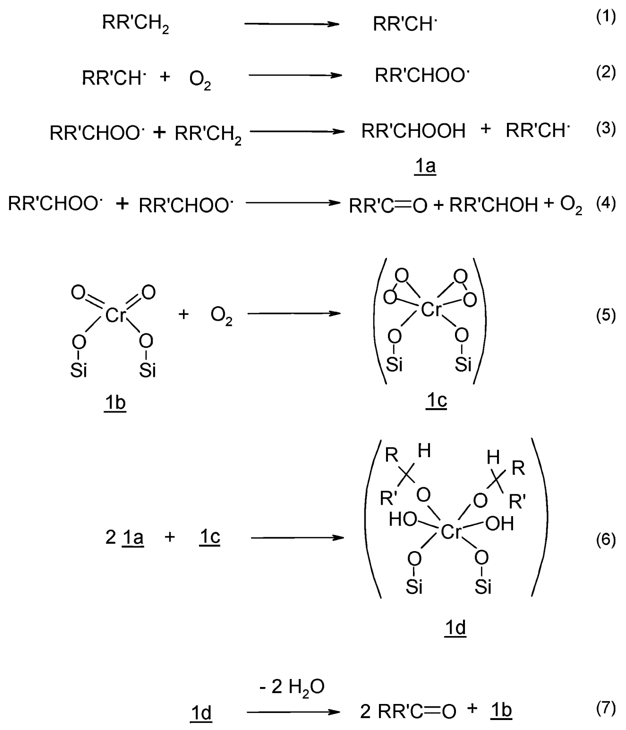
Entry	Substrate	Product	Conversion (%)	Selectivity (%)
1	 **1a**	 **2a**	65.9	96.2
2	 **1b**	 **2a**	80.1	95
3	 **1c**	 **2c**	76.6	95
4	 **1d**	 **2d**	52.4	>99
5	 **1e**	 **2e**	35.0	85
6	 **1f**	 **2f**	29.6	96

[a] *Reaction conditions*: 2 mmol substrate; *m*(CrMCM-41) = 40 mg; P_{O_2} = 2 MPa; P_{CO_2} = 9 MPa; entries 1–3 and entries 4–6, T = 80 °C and 100 °C; t = 14 h, respectively.

was oxidized, 35% conversion and 85% selectivity of 1-acenaphthenone (**2e**) was obtained (entry 5). Meanwhile, diphenylmethane (**1f**) was oxidized with 29.6% conversion and benzophenone (**2f**) selectivity of 96% was obtained (entry 6). Thus above observations suggest that the CrMCM-41/scCO$_2$ reaction system is also promising for the oxidation of other benzylic compounds.

Scheme 2 shows the hypothetical reaction pathway of oxidation of benzylic compounds by molecular oxygen catalyzed with chromium containing mesoporous catalyst. It is generally recognized that this type of oxidation proceeds *via* a radical-chain mechanism.[27] After initiation reaction (1), substrate (benzylic compound of formula: RR′CH$_2$ where R = Ph and R′ = cycloalkyl, Ph, *etc*.,) forms corresponding alkyl radicals. The alkyl hydroperoxide (1a) intermediate is produced in the sequence of propagation reactions (2) and (3), while the mutual reaction of two peroxyl radicals (4) constitutes the major chain-termination step. It has been assumed that ketone is produced at the termination step (4).

In our study, for all reactions with CrMCM-41/scCO$_2$ catalytic system, ketone was the major product. Hence, the observed reaction results with CrMCM-41 are indicative of the reaction occurring predominantly *via* a heterolytic pathway, because a homolytic pathway (Haber–Weiss mechanism) would afford alcohols as the major product. This type of mechanism is operative at propagation step. A similar mechanism is reported by Sheldon *et al.*[14] for the oxidation of alkylaromatics with molecular oxygen using CrAPO-5 catalyst. Recently Hermans *et al.*[28] also reported a comparable mechanism with silica-immobilized chromium colloids for cyclohexane autooxidation. Accordingly, we have proposed a hypothetical reaction pathway. Concurrently, chromium(VI) species (1b) in the CrMCM-41[21] catalyst may interact with molecular oxygen to produce catalytically active chromium(VI) peroxo-species (1c) (5). Similar type of chromium(VI) peroxo-species have been proposed as the active species.[12] The latter reacts with the intermediate (1a) and forms alkyl peroxochromium(VI) intermediate (1d) (6). The resulting species is then oxidized to the corresponding ketone (RR′CO) with the elimination of water (7).



Scheme 2 A hypothetical pathway of the oxidation of benzylic compounds by molecular oxygen catalyzed with CrMCM-41.

Conclusions

In summary, CrMCM-41 catalyst is found to be highly efficient for the generation and decomposition of THP to 1-tetralone in the presence of scCO$_2$. A high yield of 1-tetralone is obtained over the CrMCM-41 compared to the other metal containing nanoporous catalysts. Another important deduction is that the CrMCM-41 is resistant to leaching of chromium in the presence of scCO$_2$ medium under the present experimental conditions. Furthermore this catalytic system has been found to be suitable for the oxidation of other benzylic compounds. Therefore, mesoporous chromium catalyst is promising for various selective oxidation reactions including bulkier molecules. This approach is interesting as it ultimately could prove a useful engineering solution to the problem of solubilizing substrates in scCO$_2$ at moderate operating pressures.

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