

Cr-MCM-41-Catalyzed Selective Oxidation of Alkylarenes with TBHP

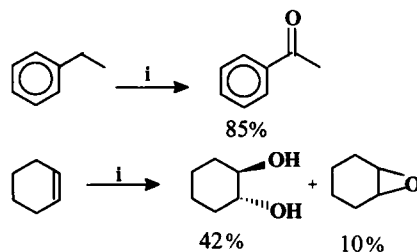
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Abstract : A mild and efficient catalytic method for benzylic oxidation of alkylarenes to the corresponding carbonyl compounds in good yields is described using a catalytic amount of reusable solid, mesoporous chromosilicate (Cr-MCM-41) and 70% tert-butyl hydroperoxide (TBHP) as oxidant. © 1997 Published by Elsevier Science Ltd.

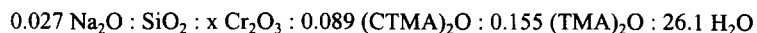
The C-H bond activation at the benzylic position by transition metal complexes under mild conditions is an important transformation in the synthetic organic chemistry. Traditionally, stoichiometric amounts of Co and Cr reagents have been used under homogeneous conditions to achieve moderate yields¹. Tedious work up and the generation of toxic chromium residues as a result of the use of a large excess of chromium reagents are the main disadvantages often encountered in the benzylic oxidations. Hence, there is a need for cleaner, catalytic alternatives which do not generate excessive amounts of inorganic salts as by-products. In this direction, recently the soluble chromium catalysts² as well as heterogeneous catalysts such as Cr-PILC³ and Cr-APO⁴ in combination with TBHP or O₂ have been developed to effect benzylic oxidations. However, these methods employ either anhydrous TBHP, the reaction fails in the case of large molecules or it takes longer time (50 h) for completion.

The synthesis of MCM-41, a new family of mesoporous molecular sieves, possessing a hexagonal array of uniform mesopores with uniform channels varying from ~ 15Å to 100Å, has stimulated considerable interest⁵. Subsequently, incorporation of transition metals such as Ti, V, Fe, Mn, Sn and Cr has been reported⁶. We wish to report here a very efficient and highly selective method for the benzylic oxidation using a new heterogeneous catalyst, Cr-MCM-41, in combination with 70% TBHP (Scheme 1).



Scheme 1: i Cr MCM-41, TBHP, MeOH, 2h

The hydrothermal synthesis⁷ of Cr-MCM-41 was carried out using gels of the following molar compositions:



where $x \leq 0.04$ and $(\text{CTMA})_2\text{O}$ and $(\text{TMA})_2\text{O}$ are organic templates.

The catalyst was characterized by XRD, TEM, DRS and ESR techniques. The BET surface area of the sample is $970 \text{ m}^2 \text{ g}^{-1}$, the pore volume being $0.6 \text{ cm}^3 \text{ g}^{-1}$.

In a typical reaction procedure, a mixture of 2-methylnaphthalene (1 g., 7.7 mmol), 70% TBHP (2 ml, 14.7 mmol) in MeOH (5 ml) was refluxed under stirring for 20 h. The catalyst was filtered off, the filtrate was washed with aq. NaHSO_3 solution to decompose any excess TBHP followed by its extraction with dichloromethane. Evaporation of the solvent furnished 2-naphthoic acid which was recrystallized from MeOH (m.p. $178 - 180^\circ\text{C}$; yield 0.665 g, 55%).

Table 1 : Catalytic oxidation of alkylarenes with 70% TBHP catalyzed by Cr-MCM-41

Entry	Substrate	t/h	Conv. ^a (%)	Products ^b (% yield ^c)
1	Toluene	20	50	Benzoic acid (45)
2	o-Xylene	18	36	o-Toluic acid (30) + Phthalic acid (5)
3	p-Xylene	20	45	p-Toluic acid (35) + Terephthalic acid (5)
4	Mesitylene	15	40	3,5-Dimethylbenzoic acid (25) + 5-Methylisophthalic acid (15)
5	2-Methylnaphthalene ^d	20	60	2-Naphthoic acid (55)
6	Ethylbenzene ^d	12	88	Acetophenone (85)
7	Tetralin	12	85	1-Tetralone (80)
8	Benzene	12	8	Hydroquinone (8)
9	Naphthalene	12	6	1-Naphthol (6)
10	Cyclohexane	12	25	Cyclohexanone (15) + Cyclohexanol (10)
11	n-Heptane	12	20	2-Heptanone (10) + 3-Heptanone (8)

^aDetermined by gas chromatography using capillary column.; ^bCharacterized by m. p., IR, ^1H & ^{13}C NMR and MS; ^cIsolated after chromatographic purification, the remaining is essentially starting material; ^dNo reaction in the absence of the catalyst, the catalyst was recovered and reused several times without any loss of activity and selectivity.

The results of C-H activation are summarized in Table 1 and Scheme 1. It is found that a variety of benzylic CH₃ groups are oxidized to acids in moderate yields while the corresponding benzylic CH₂ groups are smoothly oxidized to ketones in excellent yields (Table 1, entries 6, 7). It is also remarkable that benzene and naphthalene are selectively hydroxylated to give hydroquinone and 1-naphthol respectively although in low conversions while the corresponding aliphatic analogues are oxidized to a mixture of ketones and alcohols (entries 10, 11). A novel feature of this catalyst is that cyclohexene is converted to *trans*-1,2-diol as the major product in a single step [Scheme 1] possibly produced by the ring opening of the epoxide which is the primary product. The catalyst was recovered by simple filtration and reused successfully thrice in the oxidation of ethylbenzene without affecting the reactivity and selectivity of the process. It was further observed that the reaction failed when we carried out the oxidation of ethylbenzene with the filtrate of the catalyst at the reaction temperature, confirming that the catalyst is not leached out of the framework to catalyze under homogeneous conditions. In order to understand the mechanistic course of the reaction, toluene was oxidized with Cr-MCM-41 /TBHP system and the reaction was periodically monitored (after every 1 h.) by GC-MS and the result indicated the formation of benzyl alcohol, benzaldehyde and benzoic acid confirming that at first hydroxylation takes place at the benzylic position which then undergoes further oxidation to PhCHO and PhCOOH. However, other zeolites like TS-1 and CrS-2 under the same reaction conditions have failed to oxidize⁸ alkylarenes.

In conclusion, Cr-MCM-41 is a new and recyclable solid catalyst for the selective liquid - phase oxidation of alkyl arenes using 70% TBHP as the oxidant. The ESR spectrum of the as-synthesized Cr-MCM-41 synthesized by us shows the presence of Cr³⁺ and the corresponding calcined Cr-MCM-41 shows the presence of Cr⁵⁺ in the framework⁹ (axial symmetric signal around $g = 1.95$; line width = 250 G). It appears likely that the oxochromium (V) species present in Cr-MCM-41 framework is responsible for the C-H bond activation.

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7. In a typical experimental procedure, tetramethylammonium hydroxide (4.18 g, TMAOH.5H₂O, 99%, Aldrich) was added to cetyltrimethylammonium chloride/hydroxide [33.4 g of a 24.6 wt.% solution of CTMACl/OH⁻; 17.9 wt.% Cl⁻, 6.7% OH⁻; prepared by partial exchange of CTMACl (Aldrich, 25wt.% solution in water) over IRA - 400 (OH) ion -exchange resin] with stirring. NaOH (0.32 g) dissolved in water (12 g) was added to the stirred solution. Hisil (6.29 g, Sigma, 99% SiO₂) was added to the above mixture followed by tetramethylammonium silicate (27.2 g, 10 wt.% solution in water, 10 wt.% SiO₂, TMA:Si = 1:2). Finally, a solution of CrCl₃.6H₂O (1.6 g) dissolved in water (5 ml) was added to the above mixture. The resultant homogeneous reaction mixture (pH = 11.5) was charged into a stainless steel autoclave and heated at 413K for 6 days under static conditions to induce crystallization. After crystallization, the light green product was filtered, washed with deionized water, dried at 293K (yield 80 mass%) and calcined at 813K for 2 h under N₂ and 6 h under air. The colour of the sample after calcination was greenish - yellow. The sample was then extracted with ammonium acetate solution (1M) at 293K for 6 h. The yellow color of the sample was leached out into the filtrate and the colour of the sample remained green. The sample was again calcined at 813K in air for 4 h. The Cr content of the as-synthesized and calcined samples was about the same as that of the synthesis gel (Si/Cr = 25). However, on extraction with NH₄OAc, some Cr was lost from the sample and its Si/Cr ratio became 40.
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